

Electrostatic interactions in critical solvents

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(Dated: April 29, 2011)

Abstract

The subtle interplay between critical phenomena and electrostatics is investigated by considering the effective force acting on two parallel walls confining a near-critical binary liquid mixture with added salt. The ion-solvent coupling can turn a non-critical repulsive electrostatic force into an attractive one upon approaching the critical point. However, the effective force is eventually dominated by the critical Casimir effect, the universal properties of which are not altered by the presence of salt. This observation allows a consistent interpretation of recent experimental data.

PACS numbers: 05.70.Np, 05.70.Jk, 61.20.Qg

Introduction. Effective interactions among surfaces in contact with fluid media play a central role for a variety of topical fields in soft and condensed matter physics, cell biology, colloid and surface science, and nanotechnology. Since many relevant fluid media contain polar liquids such as water, their confining surfaces acquire an electric charge due to ion association or dissociation. As a result, electrostatic forces are expected to contribute significantly to the interactions. In addition, a strong and highly temperature-sensitive solvent-mediated effective force arises upon approaching critical points. This critical Casimir force has recently been reported for a single colloidal particle close to a wall and immersed in a binary liquid mixture near its critical demixing point [1]. This force is expected to play also a role for the aggregation of colloidal suspensions [2, 3]. Motivated by recent experiments, here we investigate the interplay between electrostatic and critical Casimir forces, which turns out to be responsible for rather unexpected effects in binary liquid mixtures with added salt. Colloids dispersed in such a solvent have been reported [2] to aggregate at a temperature difference from the critical demixing point which increases upon increasing the ionic strength, i.e., the screening of the electrostatic forces. This observation has been confirmed experimentally also for a single colloid near a wall [4]. While it was originally argued [2] that the aggregation could be completely explained in terms of a simple superposition of the critical Casimir and screened Coulomb forces (see, however, Ref. [3]), subsequent experimental results challenge this picture: An *attractive* colloid-wall interaction has been observed within a suitable temperature range even though *both* the electrostatic and the critical Casimir force are expected to be separately *repulsive* under these experimental conditions [4]. This points towards an important and yet unexplored aspect of the coupling between electrostatics and the critical fluctuations of the medium. Certain features of ion-solvent coupling near critical points were investigated in the past, such as the possibility of a micro-heterogeneous phase [5] and the influence of criticality onto the solubility of ions [6]. However, the complementary point of view, i.e., the influence of ions onto the critical fluctuations of a solvent and therefore onto the critical Casimir effect has not yet been studied. We present a minimalistic but sufficiently enriched theory which explains the aforementioned unexpected experimental results. This contribution is intended to initiate a cross fertilization between research areas which so far focused separately on the critical Casimir effect in salt-free systems or on electrostatic interactions in fluctuation-free solvents. We expect that understanding — and thus being able to use on purpose — the coupling

between the critical Casimir effect and electrostatics provides a key to push forward the topical fields mentioned above. Our findings actually reach beyond the realm of soft matter because the counterintuitive behavior en route to universality discussed here is expected to be paradigmatic for many branches of physics in which generically critical and non-critical fields are coupled.

Model. In a three-dimensional ($d = 3$) Cartesian coordinate system, we consider two parallel walls located at positions $\tilde{z} = 0$ and $\tilde{z} = \tilde{L} > 0$, respectively, with the space in between being filled by a binary liquid mixture. In this solvent cations (+) and anions (−) are dissolved. The solvent particles are all assumed to be of equal size with volume $\tilde{a}^3 > 0$ whereas the ions are considered point-like. At the dimensionless position $z := \tilde{z}/\tilde{a}$, the number densities of the solvent components are given by $\phi(z)\tilde{a}^{-3}$ and $(1 - \phi(z))\tilde{a}^{-3}$ with $0 \leq \phi \leq 1$, whereas the densities of the cations and anions are given by $\varrho_+(z)\tilde{a}^{-3}$ and $\varrho_-(z)\tilde{a}^{-3}$, respectively. The walls carry surface charge densities $\sigma_0 e \tilde{a}^{-2}$ at $z = 0$ and $\sigma_L e \tilde{a}^{-2}$ at $z = L := \tilde{L}/\tilde{a}$, where e is the elementary charge. The composition $\phi(z)$ couples to surface fields h_0 at $z = 0$ and h_L at $z = L$, where $h_{0,L} > 0$ (< 0) leads to a preferential adsorption of the solvent component with $\phi = 1$ ($= 0$). The equilibrium profiles ϕ , ϱ_+ , and ϱ_- minimize the approximate grand potential density functional $k_B T \Omega[\phi, \varrho_{\pm}]$,

$$\begin{aligned} \frac{\Omega[\phi, \varrho_{\pm}]}{A} = & \int_0^L dz \left\{ \omega_{\text{sol}}(\phi(z)) + \frac{\chi(T)}{6} \phi'(z)^2 \right. \\ & + \sum_{i=\pm} \left[\omega_{\text{ion}}^{(i)}(\varrho_i(z)) + \varrho_i(z) V_i(\phi(z)) \right] \\ & \left. + 2\pi \ell_B D(z, [\varrho_{\pm}])^2 \right\} - h_0 \phi(0) - h_L \phi(L), \end{aligned} \quad (1)$$

with $\omega_{\text{sol}}(\phi) = \phi(\ln \phi - \mu_{\phi}) + (1 - \phi) \ln(1 - \phi) + \chi(T) \phi(1 - \phi)$ and $\omega_{\text{ion}}^{(\pm)}(\varrho_{\pm}) = \varrho_{\pm}(\ln \varrho_{\pm} - 1 - \mu_{\pm})$ as the grand potential bulk densities of the solvent and the \pm -ions, respectively. Here $k_B T$ is the thermal energy, $A \tilde{a}^2$ is the area of one wall, $\mu_{\phi} k_B T$ and $\mu_{\pm} k_B T$ are the chemical potentials of the solvent composition and the \pm -ions, respectively, and $\ell_B \tilde{a} = e^2 / (4\pi \epsilon k_B T)$ is the Bjerrum length for a uniform permittivity ϵ ; a ϕ -dependent permittivity [7] corresponds to modified surface fields $h_{0,L}$ [8]. The (temperature-dependent) Flory-Huggins parameter $\chi(T) > 0$ describes the solvent-solvent interaction, which leads to a phase separation in the range $\chi(T) \geq \chi(T_c)$; the gradient term $\propto \phi'(z)^2$ accounts for the spatial variation of the solvent composition [9]. The ion-solvent interaction is given by the effective ion

potential $k_B T V_{\pm}(\phi)$ due to the solvent, with $V_{\pm}(\phi) = -\ln(1 - \phi(1 - \exp(-f_{\pm})))$ and where $f_{\pm} k_B T$ is the *difference* of the bulk solvation free energies of a \pm -ion in solvents with $\phi = 1$ and $\phi = 0$. This expression of $V_{\pm}(\phi)$ leads to a bulk phase diagram with a critical point which is shifted towards larger values of $\chi(T_c)$ as the salt concentration increases [8]. $V_{\pm}(\phi)$ is an improvement of the standard approximation ϕf_{\pm} (which it reduces to for $f_{\pm} \ll 1$) because for $f_{\pm} \gtrsim 1$ the latter leads to multiple critical points [8] which are, however, not observed experimentally. For $f_{\pm} \rightarrow \infty$ the ion potentials $V_{\pm}(\phi)$ reduce to $-\ln(1 - \phi)$ which describes the entropy loss and thus free energy increase due to the insolubility of ions in the solvent component with $\phi = 1$. The electric displacement $D(z, [\varrho_{\pm}]) e \tilde{a}^{-2}$ in Eq. (1) fulfills Gauss' law with fixed surface charges [10]: $D'(z, [\varrho_{\pm}]) = \varrho_+(z) - \varrho_-(z)$, $D(0, [\varrho_{\pm}]) = \sigma_0$, $D(L, [\varrho_{\pm}]) = -\sigma_L$. Note that $D(z, [\varrho_{\pm}])$ is generated by the \pm -ions and the surface charges $\sigma_{0,L}$, independent of ϕ . Within the present model, ions interact with the walls only electrostatically.

In order to highlight the effect of the ion-solvent coupling we focus on an approximate grand potential functional for the solvent composition alone, which is obtained by expanding $\Omega[\phi, \varrho_{\pm}]$ in Eq. (1) in terms of the order parameter $\varphi := \phi - \phi_b$ and the ion density differences $\Delta\varrho_{\pm} := \varrho_{\pm} - I$ retaining quadratic contributions as well as terms proportional to φ^3 and φ^4 . Here ϕ_b and $I = \varrho_{\pm b}$ denote the bulk solvent composition and the bulk ionic strength, respectively, corresponding to the chemical potentials μ_{ϕ} and μ_{\pm} . The minimization with respect to $\Delta\varrho_{\pm}$ leads to linear, analytically solvable Euler-Lagrange equations for $\Delta\varrho_{\pm\text{eq}}(z, [\varphi])$, which are functionals of φ . Inserting these solutions into Eq. (1) one obtains a Ginzburg-Landau-type functional

$$\begin{aligned} \frac{\mathcal{H}[\varphi]}{A} = & \int_0^L dz \left\{ U(z) \varphi(z) + \frac{t(T)}{2} \varphi(z)^2 \right. \\ & \left. + \frac{g}{24} \varphi(z)^4 + \frac{\chi(T)}{6} \varphi'(z)^2 \right\} \\ & - h_0 \varphi(0) - h_L \varphi(L) + W(L) + \mathcal{O}((\Delta\gamma)^2) \end{aligned} \quad (2)$$

with the temperature-like variable $t(T) := 1/\phi_b + 1/(1 - \phi_b) - 2\chi(T)$. Here we assume that the mixture is at its critical composition such that there is no φ^3 -term. The electrostatic effects are contained in the coupling $g := 2/\phi_b^3 + 2/(1 - \phi_b)^3 + 6I(\gamma_+^4 + \gamma_-^4)$, $\gamma_{\pm} := V'_{\pm}(\phi_b)$,

as well as in an “external” field generated by the surface charges $\sigma_{0,L}$:

$$U(z) := -\frac{\kappa\Delta\gamma}{2(1 - \exp(-2\kappa L))} \times [(\sigma_0 + \sigma_L \exp(-\kappa L)) \exp(-\kappa z) + (\sigma_L + \sigma_0 \exp(-\kappa L)) \exp(-\kappa(L - z))] \quad (3)$$

with the Debye screening length $\kappa^{-1} = (8\pi\ell_B I)^{-1/2}$ and $\Delta\gamma := \gamma_+ - \gamma_-$. The “direct”, i.e., solely ion-mediated, electrostatic interaction between the walls is given by $W(L) := (4\pi\ell_B/\kappa)P(\kappa L, \sigma_0, \sigma_L)$ where

$$P(x, y_0, y_L) := \frac{2y_0 y_L + (y_0^2 + y_L^2) \exp(-x)}{2 \sinh(x)}. \quad (4)$$

The ion-solvent coupling affects the critical point only at order $\mathcal{O}((\Delta\gamma)^2)$ [8].

Upon approaching the critical point the dimensionless bulk correlation length $\xi = \tilde{\xi}/\tilde{a} = \sqrt{\chi(T)/(3t(T))}$, which characterizes the exponential decay of the two-point correlation function, diverges. Accordingly, on the scale ξ , $U(z)$ is localized at the boundaries and therefore it merely modifies the surface fields $h_{0,L}$. Consequently \mathcal{H} turns into a standard φ^4 -theory, which describes the critical behavior of the Ising universality class [11]. Thus, within the present model, electrostatic interactions do not affect the *universal* critical behavior of the solvent.

The effective wall-wall interaction is defined by $\tilde{\omega}(L) := \omega(L)k_B T \tilde{a}^{-2}$ with $\omega(L) := (\mathcal{H}(L) - \mathcal{H}(\infty))/A$, where $\mathcal{H}(L)/A$ is the minimum of Eq. (2). In general, for the critical contribution one has $\omega(L) = \vartheta(L/\xi)/L^{d-1}$ with a universal scaling function $\vartheta(x)$, which depends only on the relative *signs* of $h_{0,L}$ [12], with $\vartheta(x \rightarrow 0) = \text{const}$ and $\vartheta(x \rightarrow \infty) = Cx^{d-1} \exp(-x)$, where C is a universal, boundary-condition-dependent constant [12].

For a sufficiently small bulk correlation length, i.e., if $\xi \ln \xi \ll L$, the term $\propto \varphi^4$ in Eq. (2) can be neglected relative to the term $\propto \varphi^2$. The resulting quadratic functional can be readily minimized and leads to the approximate effective wall-wall interaction

$$\begin{aligned} \omega(L) = & -\frac{3\xi}{\chi(T)}P(L/\xi, h_0, h_L) + \frac{4\pi\ell_B}{\kappa}P(\kappa L, \sigma_0, \sigma_L) \\ & - \Delta\gamma \frac{3\kappa\xi^2}{\chi(T)}(Q_1(\kappa L, \kappa\xi)(h_0\sigma_L + h_L\sigma_0) + \\ & Q_2(\kappa L, \kappa\xi)(h_0\sigma_0 + h_L\sigma_L)) + \mathcal{O}((\Delta\gamma)^2) \end{aligned} \quad (5)$$

with the function, which is analytical for $y > 0$,

$$Q_k(x, y) := \frac{1}{y^2 - 1} \left(\frac{y \exp(-kx/y)}{1 - \exp(-2x/y)} - \frac{\exp(-kx)}{1 - \exp(-2x)} \right). \quad (6)$$

In Eq. (5) the term $\propto P(L/\xi, h_0, h_L)$ corresponds to the contribution of the surface fields to the wall-wall interaction in the absence of ion-solvent coupling ($\Delta\gamma = 0$) whereas the term $\propto P(\kappa L, \sigma_0, \sigma_L)$ is the direct electrostatic wall-wall interaction. The term $\propto (h_0\sigma_L + h_L\sigma_0)$ is the interaction ($\propto \Delta\gamma$) of the order parameter profile close to one wall ($\propto h_{0,L}$) with the polarization of the diffuse ion layer due to the surface charge on the *opposite* wall ($\propto \sigma_{L,0}$). This coupling between the order parameter and the ion density profiles is the central result of the present analysis and has important consequences (see below). The analogous term $\propto (h_0\sigma_0 + h_L\sigma_L)$ is small.

Discussion. In the following we discuss the experiments with colloids alluded to in the Introduction. The predictions of the present model for two walls can be readily translated into those for the wall-sphere and sphere-sphere geometry by means of the Derjaguin approximation, which is applicable at separations much smaller than the sphere radii [10]. It turns out that assuming additivity of Casimir and Coulomb forces, i.e., independence of the order parameter from electrostatics, is in general insufficient to explain the experimental observations, whereas the present model, which includes ion-solvent coupling, leads to a consistent picture.

First we consider symmetric boundary conditions, $(h_0, h_L) = (-, -)$, for which the ion-solvent coupling is masked by the strong direct electrostatic repulsion. This situation has been investigated experimentally with a suspension of hydrophilic spherical colloids in a water-oil mixture [2] as well as with a single hydrophilic colloidal sphere in a similar water-oil mixture near a hydrophilic glass wall [4]. In the presence of salt aggregation [2] or strong wall-sphere attraction [4] has been observed upon approaching the critical point of the binary mixture already several Kelvin away from the critical point. Within the present model, this setting is described by $h_0 = h_L < 0$ and $\sigma_0 = \sigma_L < 0$ with the composition ϕ expressed as the mole fraction of the non-aqueous component. For a certain choice of parameters Fig. 1(a) displays the effective wall-wall interaction potential $\tilde{\omega}(L)$. Since $\Delta\gamma \gtrless 0$ corresponds to $f_+ \gtrless f_-$, a negative ion-solvent coupling strength $\Delta\gamma < 0$ describes a salt the cations of which are slightly better soluble in oil than the anions, which is expected because the oils used in the experiments, 3-methylpyridine and 2,6-dimethylpyridine (2,6-lutidine), are Lewis bases [13]. The parameters used in Fig. 1 correspond to a critical water-2,6-lutidine mixture ($\tilde{a} = 0.34\text{nm}$, $\ell_B = 2.82$) with 10mM salt ($1/\kappa = 7.73$). Far away from T_c the effective wall-wall potential $\omega(L)$ exhibits a repulsion due to the direct electrostatic wall-wall interaction.

Upon approaching T_c , $\omega(L)$ starts to develop an increasing attraction due to the critical Casimir effect. Since the change from repulsion to attraction occurs at $\kappa\xi \approx 1$, the attraction sets in only very close to the critical point if the ionic strength is small, whereas this change occurs already considerably far away from the critical point if the ionic strength is large. Due to the strong direct electrostatic wall-wall interaction between hydrophilic walls, the ion-solvent coupling does not qualitatively influence the effective wall-wall potential, so that the assumption of additivity of critical Casimir and Coulomb forces [2, 3] is justified.

The situation is different for antisymmetric boundary conditions, $(h_0, h_L) = (+, -)$, as studied experimentally in Ref. [4] using a single hydrophilic colloid near a hydrophobic glass plate. Repulsion is observed far away from as well as close to the critical point, whereas within an intermediate temperature range a strong attraction is found. The near-critical repulsion is readily understood in terms of the critical Casimir effect for antisymmetric boundary conditions and the repulsion far away from the critical point is of electrostatic origin. However, the attraction occurring in the intermediate temperature range cannot be explained within a picture without ion-solvent coupling. Figure 1(b) shows $\tilde{\omega}(L)$ for a particular choice of non-symmetric surface fields $h_0 > 0, h_L < 0$ and surface charge densities $\sigma_0, \sigma_L < 0, |\sigma_0| \ll |\sigma_L|$ corresponding to a weakly charged hydrophobic wall. Far from ($\kappa\xi \leq 0.28$) and close to ($\kappa\xi \geq 0.82$) the critical point $\tilde{\omega}(L)$ is repulsive because in Eq. (5) the terms $\propto P$ dominate. Upon increasing $\kappa\xi$ beyond 0.28, i.e., en route towards T_c , attraction occurs (see $\kappa\xi = 0.39$), which for the chosen parameters is strongest around $\kappa\xi = 0.46$ and which weakens again closer to T_c (see $\kappa\xi = 0.59$). This attraction is caused by the coupling ($\Delta\gamma < 0$) between the order parameter profile near the hydrophobic wall ($\propto h_0 > 0$) and the electrostatic potential due to the opposite, hydrophilic wall ($\propto \sigma_L < 0$). For this effect to take place it is essential that the hydrophobic wall is sufficiently weakly charged ($|\sigma_0| \ll |\sigma_L|$, see Ref. [14]).

Ion-solvent coupling manifests itself in yet another experiment described in Ref. [4], in which the surface preference of the solvent has been measured by surface plasmon resonance. It is reported that a hydrophilic surface ($h_0 < 0$) becomes less hydrophilic upon adding salt, whereas no changes have been detected for a hydrophobic surface ($h_0 > 0$). According to Eq. (2) the "external" field U for a semi-infinite system ($L \rightarrow \infty$) acts like an additional, hydrophobic surface field $\delta h_0 = -\int_0^\infty z U(z) \exp(-z/\xi) = \Delta\gamma\sigma_0\kappa\xi/(2(1+\kappa\xi)) > 0$ if $\Delta\gamma, \sigma_0 < 0$. A hydrophilic surface becomes less hydrophilic by adding salt or for $T \rightarrow T_c$,

whereas a hydrophobic surface is influenced only weakly as $|\sigma_0|$ is small.

Conclusion. We have demonstrated that even though electrolytes do not alter the universal critical behavior of polar solvents close to their critical point, the ion-solvent coupling is relevant further away, provided the direct electrostatic interaction is sufficiently weak. The crossover from an electrostatics- to a critical Casimir-dominated behavior is expected to occur near that temperature at which the bulk correlation length becomes comparable with the Debye screening length. Several experiments with monovalent ions in binary liquid mixtures can be consistently interpreted in terms of the present model, according to which the influence of the ions on the order parameter can be described by an effective “external” field proportional to a coupling parameter which measures the difference between the solubility contrasts of cations and anions in a binary solvent. The insight gained in the present study on the effects of ion-solvent coupling may provide an understanding of other situations in which critical and non-critical fields are coupled.

We thank U. Nellen, J. Dietrich, and C. Bechinger for many stimulating discussions. A.G. is supported by MIUR within “Incentivazione alla mobilità di studiosi stranieri e italiani residenti all’estero.” M.O. acknowledges support by DFG-SFB TR6/N01.

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Figures

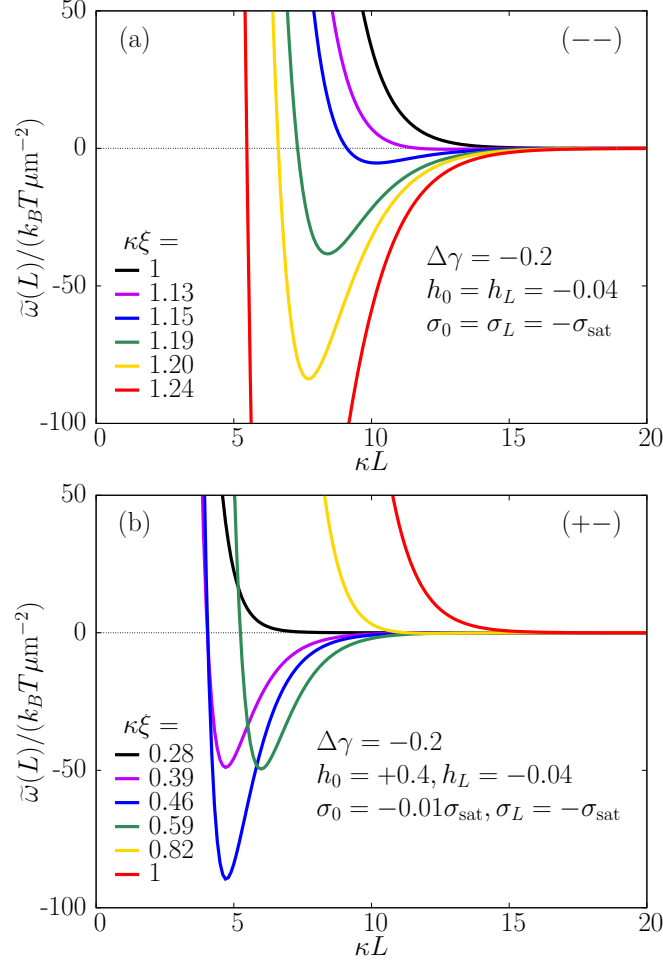


FIG. 1: Effective wall-wall interaction potential $\tilde{\omega}$ as a function of the scaled wall separation κL and the scaled bulk correlation length $\kappa\xi$ for (a) $(--)$ and (b) $(+-)$ boundary conditions; $\sigma_{\text{sat}} = \kappa/(\pi\ell_B)$ is the saturation surface charge density. For symmetric $(--)$ boundary conditions $\tilde{\omega}$ is repulsive far away from the critical point due to the direct electrostatic interaction between the like-charged walls whereas the Casimir force gives rise to an increasing attraction upon approaching the critical point. For antisymmetric $(+-)$ boundary conditions $\tilde{\omega}$ is repulsive far away from as well as close to the critical point. Attraction ($\propto \Delta\gamma$) occurs in an intermediate temperature range due to the ion-solvent coupling induced by the difference between the solubility contrasts of cations and anions in the binary solvent.